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Vibrational spectral studies of 5-methyl-2-thio uracil

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Abstract : The vibrational spectra (Infrared and Raman) of 5-methyl-2-thio uracil have been reported along with their assignments Hydrogen bonding and tautomeric behaviour of the molecule have also been discussed

Keywords : Infrared and Raman spectroscopy, vibrational frequencies, methyl thio uracil

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1. Introduction

The molecules such as cytosine, uracil and their derivatives are of immense importance because some of them are basic constituents of DNA and RNA and play an important role in constitution and properties of nucleic acids [1–4]. The recent spectroscopic studies of uracil and its derivatives have been motivated by their biological importance [2]. In many of these, it was found that the position in which sulphur was introduced, was crucial to biological activity. A complete study to vibrational spectra of 5-methyl-2-thio uracil has not been made so far. Hence the present investigation was undertaken to study the vibrational spectra of 5-methyl-2-thio uracil and to identify the frequencies of different modes of vibration in the molecule.

2. Experimental

Spec-pure grade sample of 5-methyl-2-thio uracil (here after referred as 5,2-MTU) was obtained from M/S Aldrich Chemie West Germany and used as such. Its purity was confirmed by elemental analysis and melting point determination. The infrared (IR) spectra

were recorded on Perkin-Elmer M-683 spectrophotometer in the region 200-4000 cm^{-1} (in KBr pellets) as well as 400–4000 cm^{-1} (in nujolmull, ethanol and methanol) and laser Raman spectrum was recorded on 'Spex Rama Lab.' spectrophotometer using 52 MG argon-krypton laser of wavelength 488 nm.

3. Results and discussion

The molecular structure of the compound 5,2-MTU is shown in Figure 1. The observed fundamental frequencies and their proposed assignments are given in Table 1.

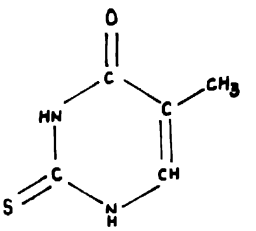

Figure 1. Molecular structure of 5,2-MTU.

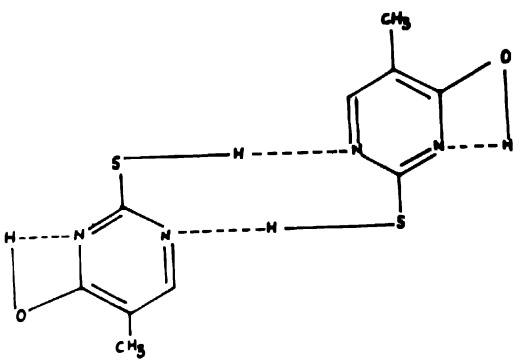

Figure 2. Hydrogen bonding 5,2-MTU.

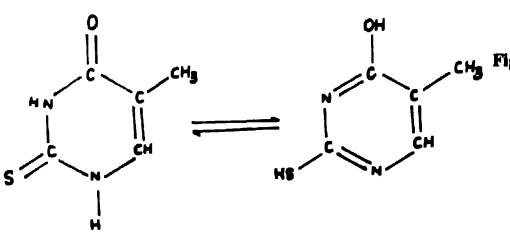

Figure 3. Tautomerism in 5,2-MTU

The correlations of IR frequencies of C–S, C=S and S–H bands are given in Table 2, while that of C = O group is given in Table 3. Hydrogen bonding and tautomeric forms of 5,2-MTU are given in Figures 2 and 3 respectively.

Table 1. Assignments of vibrational frequencies of 5,2-MTU

(All values are in cm^{-1})

Raman	IR				
	KBr	Nujol mull	Ethanol	Methanol	Assignments
75 s	–	–	–	–	Lattice vibration
88 vs	–	–	–	–	Lattice vibration
98 m	–	–	–	–	Lattice vibration
118 vs	–	–	–	–	Lattice vibration
156 s	–	–	–	–	(S–H) torsion
–	230 vw	–	–	–	γ(C–S)
–	300 vw	–	–	–	γ(C=S)
–	320 s	–	–	–	β(C–S), γ(C–OH), γ(C–CH_3)
–	–	405 w	–	–	β(C–CH_3)
–	410 vs	410 s	–	410 s	$\gamma(C_4{=}O)$
422 s	420 vw	420 m	420 w	420 w	γring
–	–	440 w	440 m	430 m	(O–H) torsion
539 m	530 s	530 s	–	–	β(C=O)
	575 w	–	–	–	γring
–	585 vs	580 vs	–	–	β(C–OH)
593 vs	–	–	–	590 vw	γring
667 m	655 m	660 m	–	–	β(C=S)
702 vvs	690 s	690 s	–	680 vw	ν(C–S)
	745 s	740 m	–	–	γring
763 vs	–	770 m	–	–	γring
–	–	–	800 vw	–	$\gamma(N_1{-}H)$
	820 vs	840 sb	–	–	γ(C–H), $\gamma(N_3{-}H)$
965 m	960 vw	–	–		ring breathing
–	1020 w	–	–	1020 w	CH_3 rocking
–	–	–	1060 vs	1060 vw	β ring
1142 m	1130 vs	1130 vs	–	1130 w	CH_3 rocking
1168 s	1160 s	1160 s	–	1160 w	ν(C=S)
1223 s	1215 vsb	1210 vs	–	–	ν(C–CH_3)
–	–	–	1280 m	–	β(O–H)
1308 w	–	–	–	1310 vw	ν(C–OH)
–	–	–	1340 m	–	ν ring
1365 vvs	1380 s	1380 s	1380 s	1380 vw	CH_3 sym. deformation ($\beta_s(CH_3)$)
1470 m	1460 s	1460 s	1460 s	1460 m	β(C–H), CH_3 asym. def ($\beta_{as}(CH_3)$)
–	1485 vw	–	–	1480 vw	CH_3 asym. deformation ($\beta_{as}(CH_3)$)
	–	–	–	1490 w	ν ring
–	1515 vw	–	–	1510 m	ν ring
–	–	–	–	1530 m	ν ring
–	1550 vs	1560 s	1560 vw	–	ν ring, β(N–H)

Table 1. *(Cont'd.)*

(All values are in cm^{-1})

Raman	IR				
	KBr	Nujol mull	Ethanol	Methanol	Assignment
1650 vs	–	1640 sb	–	1640 s	$\nu(C_4=O)$
	–	2360 m	2360 vw	–	ν(S–H)
	2820 vw	2840 s	–	–	CH_3 sym stretching
–	–	2920 vs	2920 w	2920 s	CH_3 asym stretching
–	2980 vw	–	2960 vs	2960 vw	CH_3 asym stretching
3070 vw		3080 vw	–		$\nu(C-H)$, $\nu(N_3-H)$
3250 w	3240 vw		–	–	$\nu(N_1-H)$
–			3415 vw	3420 m	ν(O–H)

where ν = stretching, w = weak,
β = in-plane bending, s = strong,
γ = out-of-plane bending, m = medium,
sym = symmetric, vs = very strong,
asym = asymmetric, vw = very weak,
def = deformation. vvs = very very strong,
sb = strong broad.

Table 2. Correlation of IR frequencies of (C–S), (C=S) and (S–H) bands

(All values are in cm^{-1})

Assignment	2-MP	4,6,2-DHMP	4,6,2-DAMP	6,5,2-ANTU	5,2-CETU	5,2-MT
ν(C–S)	470 s	460 vs	520 vs	680 s	680 vw •	690 vs
β(C–S)	328 s	330 m	–	315 s	320 m	320 s
γ(C–S)		–	–	–	–	230 vw
ν(C=S)	1190 s	1155 vsb	1182 vvs	1170 vsb	1160 w	1160 s
β(C=S)	628 ms	630 s	610 vs	630 w	635 vw	655 m
γ(C=S)	–	–	–	285 m	285 vs	300 vw
ν(S–H)	2540 wb	–	2560 w	2344 w	2360 w	2360 m

where, 2-MP = 2-mercapto pyrimidine [Ref 18]
4,6,2-DHMP = 4,6-dihydroxy-2-mercapto pyrimidine [Ref 18]
4,6,2-DAMP = 4,6-diamino-2-mercapto pyrimidine [Ref 28]
6,5,2-ANTU = 6-amino-5-nitroso-2-thio uracil [Ref 17]
5,2-CETU = 5-carbethoxy-2-thiouracil [Ref 19].

Table 3. Correlation of the infrared frequencies (cm^{-1}) of the uracil derivatives in the double bond region

Assignments	5-IU	5-FU	6-CMU	5-MU	5,2-CETU	5,2-MTU
$\nu(C_4=O)$	1645 m	1660 s	1660 s	1671 vs	1700 m	1640 s
$\beta(C_4=O)$	550 vs	560 vs	550 sb	757 vs	525 vs	530 s
$\gamma(C_4=O)$	400 m	370 m	370 m	395 ms	390 m	410 vs

where 5-IU = 5-iodo uracil [Ref 11]
5-FU = 5-fluro uracil [Ref 12]
6-CMU = 6-chloro methyl uracil [Ref. 12]
5-MU = 5-methyl uracil [Ref 14]
5,2-CETU = 5-carbethoxy-2-thio uracil [Ref. 19]

3.1 Vibrational spectra :

The molecule 5-methyl-2-thio uracil is a trisubstituted pyrimidine. The vibrational spectra (IR and Raman) have been interpreted using planar geometry and C_S point group symmetry for the molecule and the observed fundamentals have been assigned to different normal modes of vibration. The analysis of the bands and the assignments of the fundamental frequencies are made on the basis of magnitude and relative intensities of the observed bands and earlier assignments in the similar molecules.

3.1.1. Ring vibrations :

Since the molecule 5,2-MTU is trisubstituted pyrimidine, therefore, only one C–H valence oscillation is expected. A very weak IR band at 3080 cm^{-1} (in nujol) with the counterpart of Raman band at 3070 cm^{-1} has been assigned to C–H stretching mode in the title compound [5–7] It has been stated that the higher frequency corresponds to N_1–H stretching and the lower frequency to N_3–H stretching mode in uracil [5]. In view of this IR band at 3240 cm^{-1} (in KBr) with the counterpart of Raman band at 3250 cm^{-1} has been assigned to N_1–H stretching mode while the IR band at 3080 cm^{-1} (in nujol) with the corresponding Raman band at 3070 cm^{-1} may also be identified as N_3–H stretching mode

The frequency due to CH/NH stretching modes are well separated from the frequencies due to other modes The molecule under study contains only one hydrogen atom attached to the carbon atom of the ring (Figure 1). The IR value 1460 cm^{-1} in both the phases (solid and solvent) with the corresponding Raman band at 1470 cm^{-1} has been assigned to C–H in-plane bending mode. Strong band observed in IR spectra of the said molecule at 840 cm^{-1} (in nujol) is assigned to C–H out-of-plane bending mode which find support from the literature value [7,8].

It has been stated that in uracil, the band at 850 cm^{-1} is the N_3–H out-of-plane bending mode and that at 805 cm^{-1} is the N_1–H out-of-plane bending mode [9]. During the present study, a very strong IR band at 820 cm^{-1} (in KBr)/840 cm^{-1} (in nujol) has been assigned as the (N_3–H) out-of-plane mode and the weak IR band at 800 cm^{-1} (in ethanol) to the (N_1–H) out-of-plane bending mode, while the IR band observed at 1550 cm^{-1} (in KBr)/ 1560 cm^{-1} (in ethanol and methanol) has been assigned to (N–H) in-plane bending mode [4].

Some workers have identified the ring in plane bending vibration at 1054 cm^{-1} and ring breathing mode at 944 cm^{-1} in 5,6-dimethyl uracil [10]. In view of this, the IR band at 1060 cm^{-1} (in methanol and ethanol) and at 960 cm^{-1} (in KBr) alongwith corresponding Raman value 965 cm^{-1} have been assigned to ring in-plane bending and ring breathing modes respectively. A medium IR band at 1340 cm^{-1} (in ethanol) has been assigned to ring stretching vibration. These values also find support from literature value [11,12].

3.1.2. C–X vibrations :

The neutral form of uracil and its substituted derivatives have three double bonds and their stretching vibrations are expected to give rise three strong infrared bands in the

region 1600–1700 cm^{-1} [9]. The bands at 1695, 1662 and 1621 cm^{-1} in 1-methyl uracil, and those at 1690, 1676 and 1614 cm^{-1} in 5-methyl uracil, have been assigned to C_2=O, C_4=O and C=C stretching vibrations respectively [13,14], while the IR band at 1645 cm^{-1} has also been assigned to C_4=O stretching mode in 5-iodouracil [11,13]. In view of above, only one strong IR band at 1640 cm^{-1} (in nujol and methanol) has been assigned to (C_4=O) stretching mode. The bands observed at 530 and 410 cm^{-1} have been assigned to (C_4=O) in-plane bending and out-of-plane bending modes respectively [8].

The C=S stretching vibration has been calculated in the region from 1550 to 850 cm^{-1} [15]. Vir Singh *et al* [16] have assigned this mode at 1160 cm^{-1} in 5-carbethoxy-2-thiouracil. In accordance with the above discussion, the IR band at 1160 cm^{-1} (in KBr, nujol and methanol) with the counterpart of Raman band at 1168 cm^{-1} has been assigned to this mode. Seema *et al* [17] have assigned C=S in-plane bending vibration at 630 cm^{-1} in 6-amino-5-nitroso-2-thiouracil. Accordingly the IR value at 655 cm^{-1} (in KBr)/660 cm^{-1} (in nujol) with the corresponding Raman counterpart at 667 cm^{-1} is identified as C=S in-plane bending vibration. The C=S out-of-plane bending mode has been assigned at 300 cm^{-1} (in KBr) in the IR spectrum of the said molecule [16,17].

The (C–S) stretching, in-plane bending and out-of-plane bending modes have been assigned at 470, 328 and 230 cm^{-1} respectively in 2-mercaptopyrimidine [18]. In view of these assignments, the IR band observed at 690 cm^{-1} (in KBr and nujol)/680 cm^{-1} (in methanol) with the counterpart Raman band at 702 cm^{-1} has been assigned to (C–S) stretching mode, while the IR bands at 320 and 230 cm^{-1} (both in KBr) have been assigned to (C–S) in-plane bending and out-of-plane bending modes respectively in the present study [19].

The (C–CH_3) stretching, in-plane bending and out-of-plane bending modes have been assigned at 1220, 370 and 315 cm^{-1} respectively in 4,6-dihydroxy-2-methyl-pyrimidine [20]. In view of these, IR values 1215 cm^{-1} (in KBr)/1210 cm^{-1} (in nujol) with corresponding Raman value 1223 cm^{-1} have been assigned to (C–CH_3) stretching mode, while those at 405 cm^{-1} (in nujol) and 320 cm^{-1} (in KBr) correspondingly assigned to the (C–CH_3) in-plane and out-of-plane bending modes respectively.

The band at 1300 cm^{-1} has been assigned to (C–OH) stretching mode in the IR spectrum of 6-amino-5-nitroso-2-thio uracil [17]. In view of this, a very week IR band at 1310 cm^{-1} (in methanol) with the courterpart of Raman band at 1308 cm^{-1} may be assigned to (C–OH) stretching mode in the said molecule. The IR bands at 580 cm^{-1} (in nujol) and 320 cm^{-1} (in KBr) have been assigned to (C–OH) in-plane and out-of-plane bending modes respectively in the present study. These assignemts find support from literature value [12,17,21]. The presence of the O–H-vibrations is due to the tautomeric behaviour of the molecule [Figure 3].

3.1.3. Group vibrations :

3.1.3.1. CH_3 group vibrations :

Fox and Martin [22] have assigned the symmetric and asymstretching modes of methyl group at 2872 and 2962 cm^{-1} in the molecules containing methyl group CH_3 symmetric stretching modes have been assigned at 2829 and 2855 cm^{-1} in case of 5,6-dimethyl uracil and 2-amino-4-hydroxy-6-methyl pyrimidine [10,20] while the bands at 3029, 2994, 2951 and 2884 cm^{-1} have been assigned to (CH_3) asymmetric stretching modes in 5,6-dimethyl uracyl [10]. In view of the above, the IR band observed at 2820 cm^{-1} (in KBr)/2840 cm^{-1} (in nujol) has been assigned to CH_3 symmetric stretching mode while the IR bands at 2920 cm^{-1} (in nujol, ethanol and methanol) and 2980 cm^{-1} (in KBr)/2960 cm^{-1} (in ethanol and methanol) to CH_3 asymmetric stretching modes in 5,2-MTU. The symmetric, asymmetric deformation and rocking modes of methyl group in the present study are given in Table 1. These above modes find support from the literature value [10,22–25].

3.1.3.2 SH group vibrations :

Bellamy [23] has suggested the narrow range of 2590–2550 cm^{-1} for S–H stretching mode and he proposed that the bands near 2550 cm^{-1} in thio phenol were absent from their corresponding sulphides which makes it evident that this band is due to (S–H) stretching mode. The IR band at 2360 cm^{-1} (in nujol and ethanol) has been assigned to (S–H) stretching vibration during the present study, which nicely falls in the range predicted by various workers [23–27].

4. Tautomeric behaviour and hydrogen bonding

The band at 1673 cm^{-1} in uracil is assigned as C=O stretching mode [8]. Thus the IR band at 1640 cm^{-1} (in nujol and methanol) with the counterpart of the Raman band at 1650 cm^{-1} corresponds to this vibration in 5,2-MTU. However at the same time, IR band observed at 1310 cm^{-1} (in methanol) with the counterpart of Raman band at 1308 cm^{-1} has been assigned to (C–OH) stretching vibration while IR band at 3420 cm^{-1} (in methanol)/3415 cm^{-1} (in ethanol) to (O–H) stretching mode in the present study (Table 1). The presence of above said (C–OH) and (O–H) stretching modes indicates that in 5,2-MTU, the H atom of NH group present at position three has moved to position four to the ring showing tautomerism in the molecule as shown in Figure 3. Now it is also concluded that migration of H atom of NH group is not complete. The presence of the said stretching mode further suggests that the –OH group is involved in hydrogen bonding. Uracil, due to the presence of two C=O groups at position 2 and 4 and two –NH groups at position 1 and 3, generally tautomerise into a dihydroxy aromatic compound *i.e.* pyrimidine [16], but in the present case, only one (C=O) group is present at position 4, as there is a (C=S) group at position 2 in 5,2-MTU. This compound will therefore, tautomerise into a monohydroxy compound *viz*. 5-methyl-4-hydroxy-2-mercapto pyrimidine.

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